

PATENT SPECIFICATION

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(54) PEROXYGEN COMPOUNDS

(71) We INTEROX, a Société Anonyme organised under the Laws of Belgium, of 33 Rue du Prince Albert, B-1050 Brussels, Belgium, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

10 The present invention relates to a process for stabilising, by coating, particles of peroxygenned compounds, the particles of peroxygenned compounds thus obtained as well as washing or bleaching compounds containing such particles.

15 It is well known that peroxygenned compounds can be used as bleaching compounds in detergent powder mixtures. In the usual household detergents, sodium perborate tetrahydrate is generally used as a bleaching compound as it is relatively stable to decomposition in a powdered detergent medium. However, it is becoming more and more common to use cold washing and soaking techniques for linen in which sodium perborate has the disadvantage of dissolving too slowly at 20°C.

20 To rectify this disadvantage, the use has been suggested of detergent powders mixed with many other peroxygenned compounds, notably alkali metal percarbonates, perphosphates and 25 peroxymonosulphates, which have suitable dissolution rates. Now, the said peroxygenned compounds, particularly percarbonates decompose too quickly in the powdered state especially if they are stored in a humid atmosphere; furthermore, the other constituents of the cleaning compounds may activate this decomposition even more.

30 With a view to avoiding this shortcoming, it has been suggested in the French Patent 750125, filed on 30.11.1932 in the name of Oesterreichische Chemische Werke Gesellschaft that various types of stabilising agents be introduced during the manufacture of the said peroxygenned compounds by reacting salts or corresponding solid oxides with an aqueous sol-

ution of hydrogen peroxide, these stabilising agents being capable of dissolution in the aqueous solution of hydrogen peroxide and/or mixed in the solid phase with the original oxides or salts. The products thus obtained do not however have a sufficient stability; moreover, their active oxygen content is not high.

35 In order to improve the stability of the peroxygenned compounds it has also been suggested that the peroxygenned compounds be mixed in the solid phase with metaboric acid (Japanese Pat. Application 49-6760 filed on 11.9.1970 in the name of Taisho Pharmaceutical Co.). The quantities of metaboric acid used are however very high and the effect of this is that the active oxygen content of the finished product is low. Furthermore, the stability of the products obtained is not sufficient when they are mixed with other constituents of washing powders.

40 It has also been suggested that particles of peroxygenned compounds be coated by various types of stabilising agents such as mixed compounds obtained by crystallisation of sodium carbonate with other mineral salts selected from sodium bicarbonate and sodium sulphate (Belgian Pat. 813 645 filed on 12.4.1974 in the name of the Applicant). The stability of the granules thus obtained in the presence of the other constituents of the washing powders is very distinctly improved without however reaching that of the peroxygenned compounds with a high stability such as sodium perborate when stored for a very long time.

45 The Applicant has now found a means of obtaining particles of peroxygenned compounds which can be particularly stable in the presence of other constituents of washing powders, and which can have a high active oxygen content.

50 According to the present invention there is provided a peroxygenned compound coated with a solid coating agent containing at least one boric compound selected from orthoboric, metaboric and tetraboric acids.

55 According to a second aspect of the present

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invention there is provided a process for stabilising particles of peroxygenated compounds comprising the step of coating the particles with a solid coating agent containing at least one 5 boric compound selected from orthoboric, metaboric and tetraboric acids.

The best results are obtained when the coating agent contains at least one boric compound selected from metaboric and orthoboric acids.

10 The quantity of boric compound used in the coating agent is generally between 30 and 100% by weight. The best results are obtained when the quantity of boric compound is between 50 and 100% of the wt. of the coating 15 agent.

The coating agent can also contain other compounds that are known to have a stabilising effect on peroxygenated compounds. Amongst these one can use notably alkali metal phosphates and silicates.

20 Advantageously, the quantity of solid coating agent used corresponds to 0.5 to 20% by weight in relation to the weight of the peroxygenated compound to be coated; a quantity 25 of 0.5% by wt. is already sufficient to assure at least partial coating of the peroxygenated compound and to assure an increase in stability; in general there is no need to exceed a quantity of 20% in order to assure complete coating.

30 It is preferred to use quantities of coating agent corresponding to 1-15% by wt. of peroxygenated compound.

The present invention can be applied to all 35 peroxygenated compounds, whether organic or inorganic, that are present in the form of particles. It can thus be applied to particles of solid organic peroxides such as peroxidic derivatives of aliphatic, cycloaliphatic and aromatic acids. The invention is applied notably 40 to the stabilisation of particles of peroxidic derivatives of aromatic acids, such as dibenzoyl peroxide, phthaloyl peroxide, diphtaloyl peroxide, and the mono and polyperoxyacid derivatives of trimellitic, trimesic, hemimellitic, 45 pyromellitic, prehnitic and mellophanic acids.

The invention can advantageously be applied to the stabilisation of particles of peroxygenated mineral compounds such as alkali metal and alkaline earth metal peroxides and the alkali 50 metal persalts which are normally unstable.

Amongst these, the most commonly used are calcium peroxide, magnesium peroxide as well as percarbonates, perpyrophosphates, pertriphosphates, persilicates and peroxymonosulphates of alkali metals and more particularly 55 of sodium and potassium. The particles of peroxygenated compounds to be stabilised can contain one single peroxygenated compound or a mixture of peroxygenated compounds.

60 In particular, the invention can be applied very advantageously to the stabilisation of particles of sodium percarbonate.

The particles of peroxygenated compounds 65 stabilised according to the invention can contain many additives in very variable quantities

in addition to the peroxygenated compounds. Amongst these additives, it is possible to use notably stabilisers such as alkali metal or alkaline earth metal silicates. The amount of additive contained depends to a considerable extent on the use to which the peroxygenated compound is to be put, the anticipated length of storage and the nature of the peroxygenated compound. In general, such amount does not exceed 30% and preferably 15% by wt based on 75 peroxygenated compounds. Incorporating these stabilisers directly into the particles at the same time as the peroxygenated compounds is however insufficient to assure a satisfactory stability of the particles.

70 The peroxygenated compounds to which the present invention can be applied can be prepared by any method known in itself.

75 Thus, when the peroxygenated compounds are persalts, it is possible to manufacture particles of peroxygenated compounds by fluidised bed processes such as those described in British Patent No. 1300855 and British Patent No. 1403449, both in the name of Solvay and Cie. It is however impossible to use other processes 80 for manufacturing particles of persalts based for example on their crystallisation from their aqueous solutions.

85 The coating of particles of peroxygenated compounds by coating them according to the invention can be carried out by any known method.

90 A preferred technique consists of spraying onto moving particles of peroxygenated compounds an aqueous solution of the constituents of the coating agent and evaporating the water.

95 The aqueous solution is generally used at a temperature that is slightly lower than, equal to or slightly higher than that of the particles onto which it is sprayed. In general, the temperature 100 of the aqueous solution is in the range of $\pm 25^{\circ}\text{C}$ about the temperature of the particles onto which it is sprayed.

105 The concentration in the aqueous solution of the constituent(s) of the coating agent is preferably also as near as possible to the saturation concentration in the conditions under which the solution is used. In this way, the quantity of water to be evaporated is minimal.

110 The temperature at which spraying and evaporation are carried out are obviously chosen according to the nature of the peroxygenated compound. During these operations, the particles of peroxygenated compound are maintained at a lower temperature than the decomposition temperature of the peroxygenated compound and generally lower than 100°C . For evaporation, temperatures from 30 to 95°C 115 are generally used. In order to obtain a coating containing metaboric acid it is preferable to use temperatures greater than 70°C approx. and preferably from 70 to 95°C .

In order to obtain a coating containing orthoboric acid, temperatures lower than 70°C approx. are used and preferably from 30 to 70°C . In the region 120 of 70°C approx. the decomposition of the peroxygenated compound is very rapid. In order to obtain a coating containing orthoboric acid, temperatures lower than 70°C approx. are used and preferably from 30 to 70°C . In the region 125 of 70°C approx. the decomposition of the peroxygenated compound is very rapid. In order to obtain a coating containing orthoboric acid, temperatures lower than 70°C approx. are used and preferably from 30 to 70°C . In the region 130 of 70°C approx. the decomposition of the peroxygenated compound is very rapid.

of 70°C, a product is obtained which is coated with both acids at the same time.

Spraying can be carried out according to different techniques, for example in a fluidised bed, on a revolving plate, in a rotating drum or in any other similar device known in itself.

Evaporation can take place at the same time and in the same vessel as spraying or in a separate piece of apparatus. A continuous 10 operation procedure is generally used. A device such as a fluidised bed or any other device known in itself can be used. In this case, the temperature of the fluidised bed will be from 30 to 95°C.

15 The use of a fluidised bed has proved to be particularly advantageous, partly because spraying and evaporation are carried out simultaneously in the same apparatus and partly because this technique allows a more hermetic 20 and more homogenous coating to be obtained.

Any inert gas and in particular air, can be used as fluidisation gas. This gas can be heated to maintain the temperature of the fluidised bed at the desired level. It is also possible to use 25 other means of heating such as a bundle of tubes placed in the fluidised bed.

It is also possible to operate according to a similar process but discontinuously.

The coated particles obtained according to 30 the invention contain a relatively small quantity of coating agent and this ensures an active oxygen content that is always high. On the other hand, as the quantity of aqueous solution of coating agent used is small, evaporation 35 requires less energy.

The present invention also relates to washing or bleaching compounds that contain particles of at least one stabilised peroxygenated compound such as those described above.

40 Such compounds generally contain, in addition to the peroxygenated compound(s), one or more surface active agents chosen from cationic, anionic, nonionic, amphoteric or ampholytic surface active agents such as for 45 example those cited in the book "Surface

Active Agents" by A.M. Schwarz and J.W. Perry or in "Encyclopaedia of Surface Active Agents", Vol. I, 1961 and Vol. II, 1964, by I.P. Sisley and P.I. Wood and one or more detergency aids 50 called "builders" one of whose main functions is to sequester the metallic ions responsible for the hardness of the water such as for example, sodium tripolyphosphate, sodium nitrilotriacetate and the polyacrylates.

55 These compounds can also contain other substances chosen in terms of the special field of application of the composition. Amongst these, one can cite the activators of persalts, optical brighteners, foam inhibitors, enzymes, tarnishing inhibitors and soil anti-redeposition 60 agents, disinfectants, corrosion inhibitors, perfumes, dyestuffs, pH regulators, agents capable of liberating active chlorine, etc.

The particles of peroxygenated compounds 65 coated according to the preferred method of

carrying out the invention satisfy the following test. They do not lose more than 15% active oxygen after 4 weeks when they are mixed in a ratio of 2% by wt. in active oxygen with a base detergent powder that is, a detergent powder containing all the usual ingredients with the exception of any peroxygenated compound, storage being carried out at 2°C and in a relative humidity of 70% in closed cardboard boxes whose inner and outer walls are covered with a film of cellulose acetate. An example of such a base powder is given in Table II.

The examples below show the remarkable results obtained thanks to the present invention. These examples are given by way of example 80 and not by way of limitation.

EXAMPLES

Storage tests were carried out with particles of sodium percarbonate of grade A3, A4 and A5, coated by means of metaboric acid and A6 85 coated by means of orthoboric acid in conformity with the invention. By way of comparison the same storage tests and stability tests were carried out with particles of sodium percarbonate of grade R1 uncoated; and sodium perborate tetrahydrate of grade R2 uncoated.

Process for manufacturing coated particles of percarbonate

Particles of sodium percarbonate manufactured according to a fluidised bed process are used. The composition of the original particles of sodium percarbonate is given in Table I.

The preformed particles were coated by a discontinuous process in a fluidised bed.

The apparatus used consists of a cylinder 15 cm in diameter and 77 cm in height with a gas distribution plate at its base (2 mm holes), and with a bundle of tubes for heating by water vapour expanded at an effective pressure 1 kg/cm².

Initially, 3 kg of homogeneous particles of sodium percarbonate are introduced into this apparatus.

Air is passed via the gas distribution plate and an aqueous solution of boric acid is introduced by a pneumatic sprayer placed on the wall 11 cm from the bottom. According to the examples, this solution contains variable quantities of boric acid.

The height of the fluidised bed is 30 cm.

After the aqueous solution has been introduced, granules of coated sodium percarbonate are taken out of the apparatus.

The particular conditions used during the coating of sodium percarbonate are given in Table I.

Storage test in the presence of a detergent composition

The aim of the tests below is to show the stability of percarbonate particles coated according to the invention during storage in the presence of a detergent composition.

Mixtures are used with 2% active oxygen con-

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TABLE I

	Product	A ₃	A ₄	A ₅	A ₆	
5	Grade of sodium percarbonate					70
	Active oxygen content	g/kg	142	142	142	
	SiO ₂ content	g/kg	6.9	6.9	6.9	
10	Coating conditions	°C	80	78	78	75
	Temperature of the fluidised bed					
15	Fluidisation air Temp. flow (normalised)	°C Nm ³ /h	135 34	140 35	140 35	80
	Initial charge of the bed	kg	3	3	3	
20	Sprayer feed Air temperature flow (normalised) effective pressure	°C Nm ³ /h kge/cm ³	94 2.5 1.5	92 2.4 1.7	92 3.4 2.0	85
25	coating solution temperature flow boric acid concentration	°C kg/h % by wt.	93 0.605 17.5	93 0.812 17.5	93 0.900 17.5	90
30	sisting of 7g of sodium percarbonate in the form of particles coated according to the invention or uncoated particles or 10.5g of sodium perborate in the form of uncoated particles and 35 42g of a commercial detergent powder without enzymes, whose composition is given in Table II.					95

TABLE II

40	Composition of the commercial powder used for the test of storage in boxes	without enzymes	g/100g	
	soaps		10	
45	sodium alkylsulphonate		3	
	sodium alkylarylsulphonate		9	
	phosphates		43	
	silicates	(x)	7	
	Na ₂ CO ₃		2	
50	Na ₂ SO ₄		13	
	H ₂ O		12	
	various (EDTA, cellulose derivatives and optical brightener)		1	
55	(x) SiO ₂ total expressed in Na ₂ O·3SiO ₂			

After homogenisation, the mixtures are introduced into cardboard boxes (11.5 x 7 x 2 cm) covered at the front and the back with a film of cellulose acetate (permeability 550g H₂O/m² per day); the boxes thus prepared are then stored at 28°C in an atmosphere of 70% relative humidity for 4.8 and 12 weeks respectively.

Another series of boxes covered with micro-crystalline wax (permeability 5 g H₂O/m² per

day) are also prepared and stored at 35°C in an atmosphere of 80% relative humidity for 4, 8 and 12 weeks.

After each storage period, the active oxygen of the powder is measured by direct titration with KMnO₄/2 and the active oxygen loss is determined in relation to the initial active oxygen. The percentage of active oxygen loss of the particles of sodium percarbonate (PCS) that were coated is compared with percentages of active oxygen loss of the particles of sodium percarbonate that were not coated and the particles of sodium perborate (PBS) (a more stable product taken as reference) obtained in the same test conditions. The results are expressed according to the formula

$$\frac{TPCS_{\text{uncoated}} - TPCS_{\text{coated}}}{TPCS_{\text{uncoated}} - TPCS_{\text{uncoated}}} \times 100 = x \%$$

in which T denotes active oxygen loss. They express the percentage improvement in the stability of the particles of sodium percarbonate due to coating in relation to the stability of the uncoated particles of sodium perborate which is taken as a reference because most users regard it as sufficient. The method of direct titration of the active oxygen with KMnO₄/2 consists

of introducing about 10g of washing powder weighed with an accuracy of 0.01g in an Erlenmeyer flask of 750cm³, adding 100cm³ of H₂SO₄/6N, 100cm³ of distilled water and 2 drops of a silicone antifoaming agent. The vessel is then agitated until a homogeneous solution is obtained and titration is carried out

TABLE III
Results of storage tests in boxes in the presence of detergent powder free from enzymes

Characteristics of percompounds used	Products	28°C		35°C		80% relative humidity % loss active oxygen *) (% improvement in the stability in relation to that of sodium perborate)	
		4 wks	8 wks	4 wks	8 wks		
		12 wks	12 wks	4 wks	8 wks		
Particles of uncoated sodium percarbonate mean diameter = 0.255 mm	R ₁	11	16	24	25	45	68
Particles of uncoated sodium perborate. mean diameter = 0.285 mm	R ₂	2	4	5	6	14	29
Particles of sodium percarbonate coated by: 2.5% by wt.	A ₃	3.5	10 (50)*	15	10 (79)*	18 (87)*	32 (92)*
5% by wt.	A ₄	2.5	8.5	13	8.5 (87)*	15	27
10% by wt.	A ₅	1	7 (75)*	11	6 (100)*	13 (103)*	21 (121)*
orthoboric acid 5% by wt.	A ₆	3	9	14	10 (79)*	17	31

The % by weight are expressed in relation to the total weight of the granules.

with the aid of $\text{KMnO}_4 \cdot \frac{N}{2}$ until a pink colour lasting for 30 sec. is obtained. A blank titration is also carried out on an equivalent quantity of washing powder not containing a persalt. The active oxygen content of the sample, O, expressed in g. of oxygen per kg., is given by the relation

$$O = (a-b) \times \frac{1}{2} = \frac{1000}{p} \times \frac{0.016}{2}$$

10 in which:

- a, cm³, designates the volume of $\text{KMnO}_4 \cdot \frac{N}{2}$ used for the titration of the powder containing the persalt,
- b, cm³, designates the volume of $\text{KMnO}_4 \cdot \frac{N}{2}$ used for the blank titration
- p, g, designates the weight of the sample used.

The results of the tests of storage in boxes, carried out as described above on the particles 20 of sodium percarbonate coated according to the invention as well as on particles of sodium percarbonate that were not coated and on uncoated particles of sodium perborate, are given in table III.

25 These results clearly indicate the superiority of the products of the invention in relation to the uncoated particles of percarbonate and show elsewhere that the particles of sodium percarbonate coated according to the invention 30 are as stable if not more stable than those of sodium perborate (see product A5 stored at 35°C at 80% relative humidity).

WHAT WE CLAIM IS:

1. A particulate peroxygenated compound 35 coated with a solid coating agent containing at least one boron compound selected from orthoboric, metaboric and tetraboric acids.
 2. A compound as claimed in claim 1, wherein the boron compound is metaboric acid.
 3. A compound according to claim 1, characterised in that the boron compound is orthoboric acid.
 4. A compound as claimed in claims 1 and 45 2, wherein the peroxygenated compound is selected from organic peroxy acids, alkali metal or alkaline earth metal peroxides, alkali metal persalts and their mixtures.
 5. A compound as claimed in claim 3, 50 wherein the peroxygenated compound is an alkali metal persalt.
 6. A compound as claimed in any preceding claim, wherein the persalt is selected from alkali metal percarbonates, perpyrophosphates, pertriaxyl polyphosphates and peroxyomonosulphates.
 7. A compound as claimed in any preceding 55 claim, wherein the persalt is sodium percarbonate.
 8. A compound as claimed in any preceding 60 claim wherein the coating agent contains 30 to 100% by wt boron compound, in relation to the total weight of the coating agent.
 9. A compound as claimed in any preceding 65 claim, wherein the coating agent is used in a quantity corresponding to 0.5 to 20% by
- weight of the peroxygenated compound.
10. A compound as claimed in any preceding claim, wherein the coating agent is used in a quantity corresponding to 1 to 15% by weight of the peroxygenated compound. 70
 11. A particulate peroxygenated compound substantially as described herein specifically with respect to any one of the examples A3 to A6. 75
 12. A process for the stabilisation of peroxygenated compound comprising the step of coating the particles with a solid coating agent containing at least one boron compound selected from metaboric acid, orthoboric acid and tetraboric acid. 80
 13. A process as claimed in claim 12 wherein the peroxygenated compound and the coating agent are as described in any of claims 2 to 10. 85
 14. A process as claimed in any preceding claim wherein the coating is carried out by spraying an aqueous solution of the constituents of the coating agent onto the particles of the peroxygenated compound. 90
 15. A process as claimed in any preceding claim wherein the particles of the peroxygenated compound are maintained in a fluidised bed during coating. 95
 16. A process as claimed in any preceding claim wherein the temperature of the fluidised bed is maintained at from 30 to 95°C. 100
 17. A process as claimed in any preceding claim wherein the aqueous solution is used at a temperature in the range ± 25°C about the temperature of the particles into which it is sprayed. 105
 18. A process as claimed in any preceding claim wherein the concentration of the solution is near to the saturation concentration in the conditions at which it is used. 110
 19. A process as claimed in claim 12 or any of claims 14 to 18 wherein the temperature of the fluidised bed is maintained above 70°C. 115
 20. A process as claimed in claim 19 wherein the temperature of the fluidised bed is between 70 and 95°C. 120
 21. A process as claimed in claim 12 or any of claims 14 to 18, wherein the temperature of the fluidised bed is maintained below 70°C approximately. 125
 22. A process as claimed in claim 21, where in the temperature of the fluidised bed is between 30 and 70°C. 130
 23. A process for the stabilisation of particles of a peroxygenated compound according to claim 12 and substantially as described herein specifically with respect to any one of the examples. 130
 24. A particulate peroxygenated compound whenever prepared by a process as claimed in a any of claims 12 to 22. 130
 25. A washing or bleaching compound containing a particulate peroxygenated compound as claimed in any of claims 1 to 11 or 24. 130

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